Structural phase transitions of Ge$_2$Sb$_2$Te$_5$ cells with TiN electrodes using a homemade W heater tip

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The phase transitions of a Ge$_2$Sb$_2$Te$_5$ cell with a volume of $20 \times 20 \times 0.1 \, \mu m^3$ were carried out by applying a reset pulse (10 V and 50 ns) and a subsequent set pulse (5 V and 300 ns) using a homemade W heater tip fabricated by focused ion beam lithography. The phase transformation from a crystalline state to an amorphous state was confirmed by measuring the I-V curves and observation with a cross-sectional transmission electron microscope both before and after applying the reset pulse. The electron diffraction pattern obtained from the transformed area clearly showed the amorphous state. The resistance value of the transformed amorphous area was two orders higher than that of the original crystalline phase. This difference in the resistance value between the reset and set states was maintained for 20 reset/set pulse cycles. It is expected that this experimental setup can be used to evaluate the fatigue behavior of Ge$_2$Sb$_2$Te$_5$ cells with reset/set pulse cycles. © 2007 American Institute of Physics. [DOI: 10.1063/1.2709617]

Recently, wireless communication systems such as mobile telephones have grown in popularity. These systems require new memory devices with features that include low power consumption, fast read/write speeds, nonvolatility, and a high density. These requirements are a driving force in the development of new nonvolatile memory devices. Phase change random access memory (PRAM) is regarded as one of the most promising candidates for wireless communication systems. PRAM is based on a reversible phase transition between an amorphous state and a crystalline state of chalcogenide alloys. This phase transition occurs when an external electric current is applied. Among the chalcogenide alloys such as Ge$_2$Sb$_2$Te$_5$ (GST) or AgInSbTe, GST film is considered as the most feasible, with properties such as a fast reversible phase change, a minimal volume change during the crystallization, and stability of the amorphous phase at room temperature. In terms of reliability, an understanding of the degradation behavior of the electrical properties of a GST film is crucial.

Since the IBM Zurich group presented a new scanning probe-based data storage concept, many research groups have reported many potential applications for types of high-density data storage based on polymer surfaces. The studies involved the use of an atomic force microscope (AFM), an amorphous GeSb$_2$Te$_4$ film with a conductive AFM probe, and ferroelectric films with a scanning nonlinear dielectric microscope (SNDM) or AFM. In the case of an amorphous GeSb$_2$Te$_4$ film with a thickness of 20 nm, the phase transition from the amorphous state to the crystalline state was only confirmed by observing both the conductance and the topographic images before and after recording. In addition, it is expected that the commercial conductive AFM tip will be damaged during Joule heating induced by the current injected from the tip through the film.

In this study, the phase transitions of a GST cell with a volume of $20 \times 20 \times 0.1 \, \mu m^3$ using a homemade W heater tip are reported. The phase transitions were confirmed by measuring both the I-V curves and cross-sectional transmission electron microscope (TEM) observations before and after the phase transition. It is expected that the experimental setup in this study will be useful in evaluations of the fatigue behavior of GST cells.

The experimental setup equipped with an AFM utilized to observe the phase transitions of the GST cell is shown in Fig. 1(a). A TiN (100 nm)/Ti (20 nm) bottom electrode was deposited on a SiO$_2$ (1500Å)/Si substrate, followed by the deposition of a GST film with a thickness of 100 nm onto the bottom electrode via dc magnetron sputtering at room temperature. An x-ray diffraction and induced-coupled plasma atomic emission spectroscope correspondingly revealed that the GST film has an amorphous structure and chemical composition of Ge$_2$Sb$_2$Te$_5$. A two-dimensional (2D) array of the GST cell with a size of $20 \times 20 \, \mu m^2$ was fabricated using photore sist patterning, followed by a wet-etching process. The space between the GST cells was filled with a SiO$_2$ insulator layer followed by a chemical mechanical polishing (CMP) process. With the CMP process, the GST cells resurfaced. To deposit TiN top electrodes at a thickness of 100 nm using dc magnetron sputtering, the mask was carefully superimposed on the GST cells. A surface scan of the TiN top electrodes on the GST cell is shown in Fig. 1(b). As recording corresponds to amorphization through a liquid phase, protective layers are required to prevent fluidization and vaporization during the heating process. It should be noted that the TiN top electrode also played the role of a capping layer during the phase transition. The TiN material should tolerate a higher melting temperature ($T_m$) of GST ($T_m$: 632 °C; TiN $T_m$: 2950 °C) and it should also provide a conducting path for the current required for the read and write operations. The GST cell with the TiN electrodes
was annealed at 170 °C for 30 min to transform it from its initial amorphous state to a crystalline state. Therefore, all GST cells before the phase transition experiments were in a fcc crystalline state.

The phase transitions of the GST cell were carried out using an homemade W heater tip, which was fabricated using focused ion beam (FIB) (FEI Company, NONA 200) lithography. After removing the AFM tip (Cr–PtIr5 coated Si) from a commercial Si cantilever [450 μm(L) × 50 μm(W) × 2 μm(T)]; force constant: 0.2 N/m; resonance frequency: 13 kHz], a tungsten wire (diameter: 18 μm) was placed in the cantilever hole in which the original AFM tip was positioned. The adhesion problem between the W wire and the cantilever was solved by depositing a Pt film between them using a FIB. The W wire was then lithographed in a pyramidal shape, and the tip diameter was restricted to less than 100 nm. The cantilever with the homemade W heater tip was connected to a conventional AFM (Seiko Instrument, SPA-300HV).

The phase transitions from the crystalline state to the amorphous state and/or from the transformed amorphous state to the crystalline state occurred by applying a reset pulse and a set pulse, respectively, using the homemade W heater tip. The reset and set pulses were typically 10 V and 50 ns and 5 V and 300 ns in amplitude and width, respectively. First, the I-V curve of the original crystalline GST cell was measured using the homemade W heater tip in the AFM mode without applying a reset pulse. The I-V curves were then measured after applying a reset pulse and a set pulse using the W heater tip in the AFM mode. It is important to note that during all of these processes, the position of the contact point between the tip and the TiN top electrode did not change. FIB lithography was also used to prepare the TEM sample, including the aforementioned contact point after the phase transition. The beam size was focused to ~100 nm for the cross-sectional TEM observations.

Figure 2(a) shows the AFM tip of the commercial cantilever. A commercial AFM tip was initially used for Joule heating (the reset pulse) for the phase transition of the GST cell in Fig. 1(a). After several heating processes, the coated conductive layer (Cr–PtIr5) separated from the Si tip, as shown in Fig. 2(b). This was due to the thermal expansion coefficient mismatch between the adhesion layer, Cr (4.9 ×10−6/K at 300 K), and the Si tip (2.49 ×10−6/K at 300 K). This failure made it difficult to evaluate the I-V behaviors and to image the surface topography using the AFM mode before and after applying the reset pulse. Figure 2(c) shows a W heater tip fabricated using the FIB lithography process on the commercial AFM cantilever. As shown in Fig. 2(d), the W heater tip maintains its original shape regardless of the number of heating processes. Thus, it shows great thermomechanical stability during the heating process.

The I-V curve measured from the original crystalline state of the GST cell with the W heater tip before applying the reset pulse is shown in Fig. 3 with the (a) curve. The resistance value of the crystalline GST in this study, which was calculated from an “origin” linear fit, was 0.022 GΩ. The I-V curve measured after applying the reset pulse is shown in Fig. 3 with the (b) curve. It can be seen from this curve that the resistance increases significantly to 2.279 GΩ, which is two orders larger than the crystalline GST, after applying the reset pulse. It was also confirmed that the resistance value after applying the set pulse returned to the value of the crystalline state. This is shown in the inset of Fig. 3. Each resistance value of the crystalline and amorphous states was maintained until 20 reset/set pulse cycles. This result shows that the phase transition from the transformed amorphous state to the crystalline state occurred with the application of the set pulse.

Figure 4(a) shows a cross-sectional TEM image of a crystalline GST cell that does not experience the reset pulse.
In this figure, it is clear the Pt protective layer is used to protect the TiN/GST/TiN test cell from mechanical damage. The inset in Fig. 4(a) shows the electron diffraction pattern obtained from the GST cell. This pattern clearly shows that the crystalline GST cell has a fcc structure. The calculated lattice parameter, \(a_0\), is 6.042 Å, which is identical to that reported in Ref. 22. It should be noted that the \(a_0\) values of Pt and TiN are 3.923 and 4.241 Å, respectively. Figure 4(b) shows the result of the TEM observation after applying the first reset pulse. After applying the first reset pulse and subsequently measuring the \(I-V\) curve, the position of the heated area, i.e., the contact point between the tip and the TiN top electrode, could be confirmed precisely using both the AFM topography and an AFM conductive map of the TiN top electrode surface. FIB lithography for a TEM sample with a thickness of less than 100 nm, including the heated area, was carried out on the tested GST cell. The cross-sectional TEM observation results are shown in Fig. 4(b). The area marked “A” between the Pt protective layer and the TiN top electrode represents the heated area between the tip and the TiN top electrode. This area has a mound morphology of \(\sim 120 \text{ nm}^2\), which is similar to that of the W heater tip diameter. It is believed that this TiN mound forms due to the volume expansion of the amorphous GST under the TiN top electrode. Wang et al.\(^{23}\) also observed a volume expansion of an amorphous bit that was produced by the first write pulse in the crystalline matrix using AFM. It appears that another phase exists, which is the area within “B” in the crystalline GST and below the TiN mound A. The inset of Fig. 4(b) shows the electron diffraction pattern obtained from the area that appears to be the other phase. This diffraction pattern clearly shows an amorphous state; the area that appears as a separate phase is the amorphous GST transformed by the application of the reset pulse.

TEM observations of the phase transition from the amorphous state, previously transformed from the crystalline state by the application of the reset pulse, to the crystalline state again after applying the set pulse were not clear. This is easily confirmed from the \(I-V\) curve measured after applying the set pulse, however, because the state is identical to that of the original crystalline GST cell (inset of Fig. 3). Moreover, the \(I-V\) curves measured after applying the set pulse (5 V and 300 ns pulse width) were nearly identical to that of the original crystalline GST cell, as shown in the inset of Fig. 3. This result is reproducible. These experimental results clearly demonstrate that the experimental setup shown in Fig. 1(a) can be used to evaluate the fatigue behavior of GST cells. A study of the fatigue behavior of GST cells using the experimental setup shown in Fig. 1(a) is in progress and will be reported in the near future.

In summary, a phase transition of Ge\(_2\)Sb\(_2\)Te\(_5\) cell from the crystalline state to the amorphous state was carried out by applying a reset pulse using a homemade W heater tip fabricated using focused ion beam lithography. The phase transition was confirmed by measuring the \(I-V\) curves and by observing cross-sectional TEM images both before and after the applications of the reset pulse. The resistance of the transformed area was two orders higher than that of the original crystalline phase before the applications of the reset pulse. This difference in the resistance value between the reset and the set state was maintained for 20 reset/set pulse cycles, showing that a phase transition from a transformed amorphous state to a crystalline state also occurred via the application of the set pulse. Furthermore, the electron diffraction pattern obtained from the transformed area clearly showed the amorphous state.

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